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(54) Title: MELT PROCESS FORMATION OF POLYMER NANOCOMPOSITE OF EXFOLIATED LAYERED MATERIAL		
(57) Abstract This invention relates to a process of forming a polymeric nanocomposite comprising a continuous polymeric phase formed from a melt processible polymer having a melt processing temperature equal to or greater than about 220 °C and platelet particles having an average thickness equal to or less than about 50 Å, and a maximum thickness of about 100 Å having a secondary or primary ammonium cationic complex, a quaternary phosphonium cationic complex bonded to surface of said particles, the composite material formed by said process and an article formed from the composite material.		

MELT PROCESS FORMATION OF POLYMER NANOCOMPOSITE
OF EXFOLIATED LAYERED MATERIAL

5 **1. Field of the Invention**

 This invention relates to a process for forming a composite material comprising a polymer matrix having dispersed therein platelet particles, derived from swellable intercalated layered materials, and to
10 composite material formed by the process of this invention. More particularly, this invention relates to such a process where the intercalated layered material has layers which are compatible with the polymer of the matrix, such that during the process the
15 polymer-compatible layers of the intercalated material dissociate one from the other to form platelet fillers.

2. Prior Art

 A specific category of polymer nanocomposites has
20 been described as a composite material comprising a polymer matrix containing a polyamide having uniformly dispersed therein layers of silicate. Such nanocomposites are described in US Pat No. 4,739,007 and No. 4,810,734, Deutsches Pat. 3808623 A1, Japanese
25 Patent J 02 208358 A, and technical publications by the patentees (J. Inclusion Phenomena 5, (1987), 473-483; Clay Minerals, 23, (1988), 27; Polym. Preprints, 32, (April 1991), 65-66; and Polym. Prints, 28, (August 1987), 447-448.

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SUMMARY OF THE INVENTION

 This invention relates to a process for forming a polymeric composite which comprises platelet particles dispersed in a polymeric matrix which comprises the
35 steps of:

 (a) forming a "flowable mixture" comprising a melt-processible polymer and a swellable and polymer-

strength and modulus, dispersed at sub-micron size (nanoscale), impart greater mechanical reinforcement to the polymer matrix than do comparable loadings of conventional reinforcing fillers of micron size.

- 5 Nanoscale barrier layers impart lower permeability to polymers than do comparable loadings of conventional barrier fillers.

The process of this invention exhibits several advantages over monomer blending and polymerizing processes of the type described in U.S. Patent Nos. 10 4,810,734 and 4,739,007, also referred to herein as in-reactor processes. These advantages include utility for a broader range of matrix polymers; utility for a wider range of composites having the same matrix polymer due to a larger selection of 15 swelling/compatibilizing agents, each having a distinct bonding interaction with both the polymer and the platelet particle; and greater control over the molecular weight distribution of the matrix polymer. 20 For example, virtually any polymer material that can be made to flow can be compounded with nanoscale particles derived from intercalated layered materials which exfoliate during mixing in accordance with the process of this invention. In contrast, the monomer blending 25 and polymerizing processes of the prior art are restricted to polymers whose monomers are compatible with layered materials and can be polymerized effectively in the presence of the layered material. In the process of the present invention, the 30 compounding entails no special conditions specific to selected polymer molecular weight distributions. On the other hand, in-reactor processes of the prior art require special polymerization conditions for each selected molecular weight distribution due to the 35 effect of a dispersed phase on reaction mixture viscosity and polymerization kinetics. Virtually any loading of intercalated layered material is possible in

swelling/compatibilizing agents of this invention do not substantially decompose at melt processing temperatures equal to or greater than about 220°C into lower molecular weight materials which degrade polymers in the matrix or which are hazardous, either as vapors evolved during melt processing, or in articles such as films in food and drug packing.

As a further advantage of the present process, unreacted monomer can be removed prior to forming the nanocomposite. This facilitates monomer removal, for example by solvent extraction, since dispersed particles can interfere with this process.

Another aspect of this invention relates to a composite material comprising a polymeric matrix which comprises a melt processible polymer having uniformly dispersed therein platelet particles having an average thickness equal to or less than about 50 Å and preferably having a maximum thickness equal to or less than about 100 Å, said platelets having surfaces which are compatibilized with one or more "effective swelling/compatibilizing agents" selected from the group consisting of cations of the formula:

$^+\text{NH}_3\text{R}_1$, $^+\text{NH}_2\text{R}_2\text{R}_3$ and $^+\text{PR}_4\text{R}_5\text{R}_6\text{R}_7$ wherein:

R_1 is an organic radical having at least about 12 aliphatic carbon atoms;

R_2 and R_3 are the same or different and are organic radicals having at least about 5 carbon atoms; and

R_4 , R_5 , R_6 and R_7 are the same or different and are organic radicals having at least one which has at least about 8 aliphatic carbon atoms.

The polymeric compositions of this invention exhibit one or more advantages over prior art composites as for example those described in U.S. Patent Nos. 4,739,007; 2,531,396 and 4,410,734; Deutsches Pat. 3,808,623 A1; Japanese Patent No. 02208358A and EPA 0,398,551; 0,358,415; 0,352,042 and 0,398,551. For example, the composite of this

equal to or greater than about 225°C, as for example between about 225°C and about 325°C. For nylon 6, a temperature of preferably from about 250°C to about 260°C is normally employed. In the cases of amorphous thermoplastics and vulcanizable rubbers, it is a temperature at which the viscosity is sufficiently low that processing of the polymer can be performed by conventional means.

The manner in which the flowable mixture is formed is not critical and conventional methods can be employed. For example, the flowable mixture can be prepared through use of conventional polymer and additive blending means, in which the polymer is heated to a temperature sufficient to form a polymer melt and combined with the desired amount of the intercalated layered material in a granulated or powdered form in a suitable mixer, as for example an extruder, a Banbury Mixer, a Brabender mixer, a continuous mixer and the like. The polymer melt containing nano-dispersed delaminated layered material may also be formed by reactive extrusion in which the layered material is initially dispersed as aggregates or at the nanoscale in a liquid or solid monomer and this monomer is subsequently polymerized in an extruder or the like. Such monomer or other reactive solid or liquid dispersion can be injected into a polymer melt containing one or more polymers in an extruder or other mixing device. The injected liquid may result in new polymer or in chain extension or grafting to the polymer initially in the melt. Alternatively, the polymer may be granulated and dry mixed with the intercalated layered material, and thereafter, the composition may be heated in a mixer until the polymer is melted forming the flowable mixture. As described above, the flowable mixture is, in the second step, subjected to a shear in a mixer sufficient to form the

Swellable layered materials are materials comprising planar layers arrayed in a coherent, coplanar structure, where the bonding within the layers, is stronger than the bonding between the layers such that the materials exhibit increased interlayer spacing in their intercalation compounds. The effective swelling/compatibilizing agents may be introduced into the interlayer spaces by either insertion, in the case of neutral molecules, or ion exchange, in the case of ions. The effective swelling/compatibilizing agents may be introduced in the form of a solid, liquid, gas, or solute. The effective swelling/compatibilizing agents may be introduced into the spaces between every layer, nearly every layer, or a large fraction of the layers of the layered material such that the resulting platelet particles comprise less than about 10 layers in thickness. The platelet particles are preferably less than about 8 layers in thickness, more preferably less than about 5 layers in thickness, and most preferably, about 1 or 2 layers in thickness.

Any swellable layered material having the above referenced characteristics may be used in the practice of this invention. Useful swellable layered materials include phyllosilicates. Illustrative of such materials are smectite clay minerals such as montmorillonite, nontronite, beidellite, volkonskoite, hectorite, saponite, sauconite, magadiite, and kenyaite; vermiculite; and the like. Other useful layered materials include illite minerals such as ledikite and admixtures of illites with the clay minerals named above. Other useful layered materials, particularly useful with anionic polymers, are the layered double hydroxides, such as $\text{Mg}_6\text{Al}_{3,4}(\text{OH})_{18,8}(\text{CO}_3)_{1,7}\cdot\text{H}_2\text{O}$ (see W.T. Reichle, J. Catal., 94 (12985) 547), which have positively charged layers and exchangeable anions in the interlayer spaces. Other layered

performance of the intercalated layered material in the practice of this invention and interlayer spacing must be sufficiently large to allow for the desired exfoliation of the layers during the process. As used
5 herein the "inter-layer spacing" refers to the distance between the faces of the layers as they are assembled in the intercalated material before any delamination (or exfoliation) takes place. The preferred clay materials generally include interlayer or exchangeable
10 cations such as Na^+ , Ca^{+2} , K^+ , Mg^{+2} and the like. In this state, these materials do not delaminate in host polymer melts regardless of mixing, because their interlayer spacings are usually equal to or less than about 4 Å consequently the interlayer cohesive energy
15 is relatively strong. Moreover, the metal cations do not aid compatibility between layers and the polymer melt. In the preferred embodiments, these layered materials are intercalated by swelling agents of sufficient size to increase interlayer spacing to the
20 desired extent. In general, the interlayer spacing should be at least about 4 Å, as determined by x-ray diffraction, in order to facilitate delamination of the layered material at the nanoscale. In the preferred embodiments of the invention, the interlayer spacing is
25 at least about 6 Å and more preferred interlayer spacings are at least about 8 Å. Most preferred interlayer spacings are equal to or greater than about 10 Å. In the embodiments of choice interlayer spacings are at least about 15 Å.

30 In order to further facilitate delamination of layered materials into platelet particles and prevent reaggregation of the particles, these layers are intercalated by the effective swelling/compatibilizing agents of this invention. These agents consist of a
35 portion which bonds to the surface of the layers and another portion which bonds or interacts favorably with the polymer in the matrix. The agent of this invention

R_1 is an organic radical having at least about 12 aliphatic carbon atoms;

R_2 and R_3 are the same or different and are organic radicals having at least about 5 carbon atoms; and

5 R_4 , R_5 , R_6 and R_7 are the same or different and are organic radicals of which at least one has about 8 aliphatic carbon atoms.

Such ammonium and phosphonium radicals are well known in the art and can be derived from the
10 corresponding amines and phosphines using conventional processors.

Illustrative of such suitable R_1 , R_2 , R_3 , R_4 , R_5 , R_6 AND R_7 groups are suitable organic radical as for example alkyl, such as methyl, ethyl, octyl, nonyl,
15 tert-butyl, neopentyl, isopropyl, sec-butyl, dodecyl and the like; alkenyl such as 1-propenyl, 1-butenyl, 1-pentenyl, 1-hexenyl, 1-heptenyl, 1-octenyl and the like; alkoxy such as propoxy, butoxy, methoxy, isopropoxy, pentoxy, nonoxy, ethoxy, octoxy, and the
20 like; cycloalkenyl such as cyclohexenyl, cyclopentenyl and the like; alkanoylalkyl such as butanoyloctadecyl, pentanoylnonadecyl, octanoyl pentadecyl, ethanoylundecyl, propanoyl hexadecyl and the like; amino; aryl such as phenyl, naphthyl and the like;
25 alkylaryl such as nonylphenyl, octylphenyl tert-butylphenyl and like; alkylaminoalkyl, such as methylamino octadecyl, ethylamino pentadecyl, butylamino nonadecyl and the like; dialkylaminoalkyl, such as dimethylamino octadecyl, methylethylamino
30 nonadecyl and the like; arylaminoalkyl such as phenylamino octadecyl, p-methylphenylamino nonadecyl and the like; diarylaminoalkyl, such as diphenylamino pentadecyl, p-nitrophenyl-p'-methylphenylamino octadecyl and the like; alkylarylaminomalkyl, such as
35 2-phenyl-4-methylamino pentadecyl and the like; alkylsulfinyl, alkylsulfonyl, alkylthio, arylthio, arylsulfinyl, and arylsulfonyl such as butylthio

swelling/compatibilizing agents are reactive with a polymeric component in the polymer to form covalent bonds between matrix the swelling/compatibilizing agent and the polymeric component, or, in the case of
5 secondary ammonium cations and quaternary phosphonium cations may include both reactive and non-reactive moieties. Useful reactive swelling/compatibilizing agents includes one or more substituents selected from the group consisting of organic radicals which are
10 compatible with the polymer forming the composite and which has substituents which are reactive with the polymer such as nucleophilic or electrophilic moieties which are capable of electrophilic or nucleophilic displacement reactions coupling and ring opening
15 reactions and the like as for example amino, carboxy, carboxylic acid, oxide, alkenyl, acetylene, acylhalide, acyloxy, hydroxy, isocyanato, ureido, halo, epoxy, epichlorohydrin, sulfonyl halide, mercapto, ester, and the like.

20 Swelling/compatibilizing agents containing reactive substituents are well known in the art and are selected for particular classes of matrix polymers based on the reactivity and specifically of the reactive moiety. For example polyamides are acid
25 terminated and/or amine terminated and polyesters are acid terminated or hydroxy terminated. Thereof, reactive function groups which react with acid, amine or hydroxy functions to form covalent bonds can be conveniently used with polyesters and polyamides.
30 Specific reactive functions such as $-NH_2$, $-N=C=O$, $-CONH_2$, $-OH$, OM^+ (where M is a metal cation), $-C(O)X$ (where X is Cl, Br, or I) and the like in the reactive silane compound react with reactive functionalities contained in polyesters and polyamide. Similarly,
35 swelling, compatibilizing agents of this invention containing functions such as $-NH_2$, CH_2-X (where X is Cl, Br or I), $-CH_2=CH_2$, $-SH$, SM^+ (where M^+ is a metal cation

that are polymer-reactive are protonated 11-(hexylamino)undecanoic acid and bis(8-hexanol) amine.

Organic radicals preferred in phosphonium cations are disclosed in U.S. Patent No. 4,136,103. They preferably include at least one having 8 or more carbons. More preferably, they include at least 2 groups of 8 or more carbons or at least one group of 16 or more carbons. Most preferably they include at least one group of 18 or more carbons. Illustrative of these phosphonium cations are octyltributylphosphonium, hexadecyltributylphosphonium and vinylbenzyltriethylphosphonium. One or more of the moieties may be polymer-reactive. Illustrative of preferred phosphonium cations having reactive moieties are bis-(dimethylaminopropyl) dodecyl isobutylphosphonium and bis-(hydroxypropyl) octadecylisabutyl phosphonium).

The swelling/compatibilizing agents are preferably selected from the group consisting of primary and secondary ammonium cationic complexes of the formula:



wherein:

R_1 is an aliphatic radical having at least about 15 aliphatic carbon atoms, said radical optionally including one or more heteroatoms, carbonyl functions or a combination thereof; and

R_2 and R_3 are the same or different and are aliphatic radicals having at least about four aliphatic carbon atoms, or R_2 and R_3 together may form a divalent aliphatic chain having at least about four aliphatic carbon atoms forming an alicyclic structure, said radical or chain optionally including one or more heteroatoms, carbonyl function or a combination thereof.

In the preferred embodiments of the invention R_1 is an aliphatic radical having at least about 18 carbon atoms, said aliphatic radical optionally includes one

Layered material may be derivatized by a single swelling/compatibilizing agent of this invention, or by a mixture of such agents, or by a mixture of one or more thermally stable onium cations with one or more other swelling/compatibilizing agents such as one or more organo silanes or quaternary or tertiary ammonium radicals as for example such swelling/compatibilizing agents which have moieties which are compatible with and which are optionally reactive with the polymer forming the matrix. In the preferred embodiments of the invention the moieties are such that the swelling and compatibilizing agents are lipophilic such that the surface tension, at 20°C, or the derivatized particle is preferably less than or equal to about 55 dyne/cm. More preferably, between about 55 and 15 dyne/cm, and preferably between 45 and 20 dyne/cm, as determined by measuring the contact angles made by sessile drops of liquids on the solid surfaces.

Illustrative of such optional onium compounds are oxonium compounds of the formula:



wherein X^+ is a tertiary or quaternary ammonium radical and R_{14} is an radical as for example substituted or unsubstituted alkyl, cycloalkenyl, cycloalkyl, aryl, or alkylaryl, either unsubstituted or substituted with amino, alkylamino, dialkylamino, nitro, azido, alkenyl, alkoxy, cycloalkyl, cycloalkenyl, alkanoyl, alkylthio, alkyl, aryloxy, arylalkylamino, alkylamino, arylamino, dialkylamino, diarylamino, aryl, alkylsulfinyl, aryloxy, alkylsulfinyl, alkylsulfonyl, arylthio, arylsulfinyl, alkoxycarbonyl, arylsulfonyl, alkylsilane, and a moiety of the formula:



wherein R_{16} is alkyl, cycloalkyl, or aryl, R_{15} is hydrogen, alkyl, or aryl, q is an integer equal to or greater than 1 and Z is $-O-$ or $-NR_{17}-$, where R_{17} is hydrogen, alkyl, aryl or alkylsilane. Illustrative of

about 200 mmole/100 g. In the case of the preferred smectite clay minerals, the more preferred amounts are from about 80 mmole/100 g to about 120 mmole/100 g of layered material.

5 Swellable and polymer-compatible intercalated layered material can be formed by any method. Preferably such materials are formed by intercalation of suitable agents or agents in the interlayer spaces of the swellable layered material by any suitable
10 method. The swelling/compatibilizing agents are introduced into the interlayer spaces of the swellable layered material by any suitable method as, for example, by either insertion of neutral molecules or by ion exchange with ionic molecules, using conventional
15 procedures. Insertion of neutral molecules may be performed by exposing finely divided layered material to intercalants in the form of a gas, neat liquid, finely divided solid, or solute in a solvent which, preferably swells the layered material. Insertion is
20 generally aided by exposure of the mixture of intercalant and layered material to heat, ultrasonic cavitation, or microwaves. Ion exchange by ionic molecules may be performed by suspending the layered material in a relatively volatile liquid which is
25 capable of both exfoliating and dispersing the layers of the intercalated layered material and dissolving a salt of the ionic intercalant as well as the resulting salt of the ion displaced from the layered material (e.g., Na^+ , Mg^{+2} , Ca^{+2}), adding the salt of the ionic
30 intercalant, and removing the layered material (now complexed with the new intercalant) from the liquid (now containing the dissolved salt of the displaced ion). For example, swellable layered minerals such as montmorillonite and hectorite (having primarily Na^+
35 cations in the interlayer spaces) intercalate water to the point that the layers are exfoliated and dispersed uniformly in water. Dispersion in water is generally

dioxane, glyme, diglyme, dimethylsulfoxide, methylethylketone, and the like, or by treating an aqueous suspension of a layered material with water-soluble silane coupling agents such as trialkoxysilanes followed by interaction with an agent of this invention. In the preferred embodiments, silane intercalated swellable/polymer compatible intercalated layered material is formed as follows: Layered materials intercalated with the swelling/compatibilizing agent of this invention, preferably prepared as described above are suspended and swollen in a swelling organic liquid and treated with a trialkoxysilane. For example, montmorillonite intercalated with octadecylammonium cation, at about 80 mmole of ammonium cation/100 g mineral, is combined with dioxane to form a 5% by weight suspension which is heated to 60°C and combined with a dioxane solution of aminoethylaminopropyl trimethoxysilane, such that the ratio of silane to mineral is about 20 mmole/100 g. The silane displaces the ammonium cation quantitatively to form a mixed intercalated layered material having about 60 mmole of ammonium cation and 20 mmole of silane per 100 g of mineral layers.

In the preferred embodiments of this invention, swellable and polymer-compatible intercalated layered compounds include montmorillonite (Gelwhite HNF, Southern Clay Products) complexed with octadecylammonium cation (100 mmole/100 g mineral), montmorillonite complexed (Volclay, American Colloids Company) with dipentylammonium cation (100 mmole/100 g), synthetic hectorite (Laponite S, Laporte Industries) complexed with dioctylammonium cation (80 mmole/100 g), commercially available organo clay (Claytone APA^R, Southern Clay Products), montmorillonite complexed with octadecylammonium cation (about 80 mmole/g) and derivatized with

gamma phase) or limit spherulite size which reduces haze and increases optical clarity. In general, the amount of material employed is less than about 60% by weight of the mixture. The amount of material employed
5 is preferably from about 0.01% to about 20 % by weight of the mixture, more preferably from about 0.05% to about 10% by weight of the mixture, and most preferably from about 0.05% to about 8% by weight.

The second essential ingredient of the flowable
10 mixture is a melt processible polymer. Polymers for use in the process of this invention may vary widely, the only requirement is that they are melt processible. As used herein, a "polymer" is a substance composed of ten or more recurring monomeric units which may be the
15 same or different which is melt processible, preferably at a temperature equal to or greater than about 220°C, preferably equal to or greater than about 230°C, more preferably from about 230° to about 320°C, and most preferably from about 240° to about 290°. In the
20 preferred embodiments of the invention, the polymer includes at least twenty recurring monomeric units. The upper limit to the number of recurring monomeric units is not critical, provided that the melt index of the polymer under use conditions is such that the
25 polymer forms a flowable mixture. More preferably, the polymer includes at least about 30 recurring monomeric units. In the most preferred embodiments of this invention the number of recurring units is such that the polymer has a melt index of from about 0.01 to
30 about 12 grams per 10 minutes at the processing temperature.

Useful polymers are thermoplastic polymers or mixtures thereof, and vulcanizable and thermoplastic rubbers. Thermoplastic resins for use in the practice
35 of this invention may vary widely. Illustrative of useful thermoplastic resins are polylactones such as poly(pivalolactone), poly(caprolactone) and the like;

polymerization product of diols such as glycerin, trimethylol-propane, 1,2,6-hexanetriol, and the like with a polyisocyanate such as 2,4-tolylene diisocyanate, 2,6-tolylene diisocyanate, 4,4'-diphenylmethane diisocyanate, 1,6-hexamethylene diisocyanate, 4,4'-dicyclohexylmethane diisocyanate and the like; and polysulfones such as the reaction product of the sodium salt of 2,2-bis(4-hydroxyphenyl) propane and 4,4'-dichlorodiphenyl sulfone; furan resins such as poly(furan); cellulose ester plastics such as cellulose acetate, cellulose acetate butyrate, cellulose propionate and the like; silicones such as poly(dimethyl siloxane), poly(dimethyl siloxane), poly(dimethyl siloxane co-phenylmethyl siloxane), and the like; protein plastics; and blends of two or more of the foregoing.

Vulcanizable and thermoplastic rubbers useful in the practice of this invention may also vary widely. Illustrative of such rubbers are brominated butyl rubber, chlorinated butyl rubber, polyurethane elastomers, fluoroelastomers, polyester elastomers, butadiene/acrylonitrile elastomers, silicone elastomers, poly(butadiene), poly(isobutylene), ethylene-propylene copolymers, ethylene-propylene-diene terpolymers, sulfonated ethylene-propylene-diene terpolymers, poly(chloroprene), poly(2,3-dimethylbutadiene), poly(butadiene-pentadiene), chlorosulphonated poly(ethylenes), poly(sulfide) elastomers, block copolymers, made up of segments of glassy or crystalline blocks such as poly(styrene), poly(vinyl-toluene), poly(t-butyl styrene), polyester and the like and the elastomeric blocks such as poly(butadiene), poly(isoprene), ethylene-propylene copolymers, ethylene-butylene copolymers, polyether ester and the like as for example the copolymers in poly(styrene)-poly(butadiene)-poly(styrene) block

skill in the art, accordingly, only the preferred optional components will be described herein in detail.

In the second step of the process of this invention, the flowable mixture is subjected to a shear having an "effective shear rate". As used herein, an "effective shear rate" is a shear rate [as shear rate is defined in Ferdinand Rodriguez, "Principles of Polymers Systems", McGraw-Hill Book Company, New York (1982)] which is effective to delaminate at least about 90% by weight of the intercalated material to form platelet particles described above, and provide a composition comprising a polymeric matrix having platelet particles substantially homogeneously dispersed therein. In the preferred embodiments of the invention, the shear rate is greater than about 10 sec^{-1} . In these preferred embodiments of the invention, the upper limit for the shear rate is not critical provided that the shear rate is not so high as to physically degrade the polymer. In the particularly preferred embodiments of the invention, the shear rate is from greater than about 10 sec^{-1} to about $20,000 \text{ sec}^{-1}$, and in the most preferred embodiments of the invention the shear rate is from about 100 sec^{-1} to about $10,000 \text{ sec}^{-1}$.

Any method which can be used to apply a shear to a flowable mixture or any polymer melt can be used. The shearing action can be provided by any appropriate method, as for example by mechanical means, by thermal shock, by pressure alteration, or by ultrasonics. Methods useful in shearing melts are known in the art, and will not be described in great detail. In particularly useful procedures, the flowable polymer mixture is sheared by mechanical methods in which portions of the melt are caused to flow past other portions of the mixture by use of mechanical means such as stirrers, Banbury® type mixers, Brabender® type mixers, long continuous mixers, and extrudes. Another

matrix. As used herein, "platelet particles" are particles having two relatively flat opposite faces wherein the thickness of which is the distance between the faces, which is relatively small compared to the size of the faces. As formed by this process, the platelet particles dispersed in matrix polymers have the thickness of the individual layers, or small multiples less than about 10, preferably less than about 5 and more preferably less than about 3 of the layers, and still more preferably 1 or 2 layers. In the preferred embodiments of this invention, intercalation of every interlayer space is complete so that all or substantially all individual layers delaminate one from the other to form separate platelet particles. In cases where intercalation is incomplete between some layers, those layers will not delaminate in the polymer melt, and will form platelet particles comprising those layers in a coplanar aggregate. These latter platelet particles still constitute nanoscale and nanodispersed fillers and provide enhanced properties over and above those provided by conventional micro-scale fillers, as long as they are less than about 10 layers thick and preferably less than 5 layers thick. The other dimensions of the platelet particles may vary greatly, but in the case of particles derived from clay minerals, the particle faces are roughly round or oblong having average diameters between about 10,000 Å and about 50 Å, such that the aspect ratio length/thickness ranges from about 1000 to about 1. For the purposes of the present invention, the average diameter is defined as the diameter of a circle having an area equal to the surface area of one broad surface face of the platelet shaped particle. The average diameter is determined from particle surface area as measured with a Leitz Texture Analyzer System in a fully computerized and automated mode. In the preferred embodiments of the

etermined from estimates based on transmission electron microscopy.

The process of this invention is preferably carried out in the absence of air, as for example in the presence of an inert gas, such as, argon, neon, nitrogen or the like. The process can be carried out in a batchwise or discontinuous fashion, as for example, carrying out the process in a sealed container. Alternatively, the process can be carried out in a continuous fashion in a single processing zone, as for example by use of an extruder, from which air is largely excluded, or in a plurality of such reaction zones in series or parallel.

The nanocomposites of this invention exhibit useful properties which are superior to those predicted by U.S. Patent Nos. 4,739,007 and 5,810,734. Various useful performance indices can be devised in order to jointly assess different performance aspects using a single number. Depending upon the nature of the devised index, comparisons can be made either between samples containing the same loading of layered material or the index can be more broadly applied to polymers having different loadings of clay. For example, the effect of adding nanoscale particulate fillers dispersed platelet particles to a polymer typically increases tensile modulus and ultimate tensile strength while decreasing ultimate elongation. In the case where combinations of high modulus (Y) and high ultimate elongation ($\Delta L/L$) are required, a useful performance index for comparing samples with similar particulate loading is $Y(\Delta L/L)$. Likewise, when tensile strength (S) combined with high ultimate elongation is sought, a useful performance index for comparing samples with similar loading levels is $S(\Delta L/L)$. The preferred embodiments of the present invention provide a $Y(\Delta L/L)$ of above about 660 MPa (preferably equal to or greater than about 800 MPa more preferably equal to

only weakly bonded to the matrix polymer. This function is best performed by secondary ammonium compounds of the formula $^+\text{NH}_3\text{R}_1$, primary ammonium compounds of the formula: $^+\text{NH}_2\text{R}_2\text{R}_3$, and quaternary phosphonium compounds of the formula $^+\text{PR}_4\text{R}_5\text{R}_6\text{R}_7$, of the type having a lipophilic moiety such that the surface tension, at 20°C, of the derivatized particle is less than about 55 dyne/cm, preferably between about 55 and 15 dyne/cm, and more preferably between about 45 and 20 dyne/cm, as determined by measuring the contact angles made by sessile drops of liquids on solid surfaces. Illustrative of these preferred secondary ammonium compounds, primary ammonium compounds and quaternary phosphonium of the formula:

15 $^+\text{NH}_3\text{R}_1$, $\text{NH}_2\text{R}_2\text{R}_3$ or $^+\text{PR}_4\text{R}_5\text{R}_6\text{R}_7$
wherein R_1 , at least one of R_2 and R_3 or at least one of R_4 , R_5 , R_6 and R_7 is alkyl, alkenyl, cycloalkyl, alkoxyalkyl, alkynyl, phenylalkyl, alkoxyphenyl, alkenylphenyl, phenylalkenyl, phenylalkynyl, 20 alkynylphenyl or the like, preferably alkyl which include sufficient number of aliphatic carbon atoms such that the radical on the particle has a surface tension at 20°C of less than about 55 dyne/cm.

The nanocomposite compositions according to the invention are thermoplastic and, in some cases, 25 vulcanizable materials from which molded articles of manufacture having valuable properties can be produced by conventional shaping processes, such as melt spinning, casting, vacuum molding, sheet molding, 30 injection molding and extruding. Examples of such molded articles are components for technical equipment, apparatus castings, household equipment, sports equipment, bottles, containers, components for the electrical and electronics industries, car components, 35 circuits, fibers, semi-finished products which can be shaped by machining and the like. The use of the materials for coating articles by means of powder

preferably from about 20 to about 100 microns and most preferably from about 25 to about 75 microns in thickness. In the film, the major plane of the platelet fillers is substantially parallel to the major plane of the film. The extent of parallelism of particles and film can be determined by X-ray analysis. X-ray analysis is a useful way to described the crystallinity and orientation of polymer crystals and the orientation of platelet particles. A convenient method of X-ray analysis is that described in Hernans, P.H. and Weidinger A., Makromol Chemie, Vol. 44, pp. 24-36 (1961), hereby incorporated by reference.

For the purpose of the present invention Op, the platelet orientation factor, is an indication of the platelet particle orientation in the film. The Op was determined by making azimuthal scans from densitometer tracings of the X-ray photographs which were obtained by exposing the edge of the film to the incident X-rays. The angle is the angle between the reference direction, the normal to the film, and the normal to the plane of interest, the major plane of the platelet. The Op values were calculated as the average cosine square ($\langle \cos^2 \rangle$) for the normal to the flat faces of the platelet particles. An Op of 1.0 indicates that the faces of the platelets are completely parallel to the plane of the film. An Op of 0.0 indicates that the faces of the platelets are perpendicular to the plane of the film. The Op of the platelets in the film of the present invention is preferably from about 0.70 to about 1.0, more preferably from about 0.90 to about 1.0 and most preferably from about 0.95 to about 1.0. Such preferred orientation of platelet particles results in enhanced barrier properties and increased tare strength.

The homogeneously distributed platelet particles and polymer are formed into a film by suitable film-forming methods. Typically, the composition is melted

obtained from Southern Clay Products) at about 80°C with high shear mixing. The stoichiometry of the exchange reaction was 0.125 mole of the dipentyl ammonium chloride per 100g of clay. The organoclay flocculated immediately and, after standing overnight at room temperature, was collected by filtration. The organoclay was washed 4 times with hot water until free of chloride ions, dried in air at 120°C, ground to pass through a 75 micron sieve, and further dried at 120°C (full vacuum) for 18 hours just prior to compounding. Samples of the montmorillonite-dipentyl ammonium cation complex powder were evaluated by thermogravimetric analysis at a heating rate of 10 degree C per minute in inert atmosphere. The apparent decomposition temperature and the extent of decomposition during heating to 300°C are set forth in Table 1.

TABLE 1
THERMOGRAVIMETRIC ANALYSIS OF
INTERCALATED MONTMORILLONITES

Exp. No.	swelling/compatibilizing cation	decomposition onset temperature (C)	weight loss between 100 and 300°C (% of total onium ion content)
1	dipentyl ammonium (secondary)	275	5.6

a. Claytone APA (montmorillonite complex) obtained from Southern Clay Products.

According to the results summarized in Table 1, the montmorillonite complex of the secondary ammonium cation was more thermally stable than either the tertiary or the quaternary ammonium cation complexes. The montmorillonite-dipentyl ammonium cation complex powder was dry mixed with nylon 6 pellets, and this mixture was extruded using a Leistritz twinscrew extruder equipped with general purpose screws. The

analysis together with the thermogravimetric results from Table 1 of Example 1 are set forth in Table 3.

TABLE 3

THERMOGRAVIMETRIC ANALYSIS OF
INTERCALATED MONTMORILLONITES

Exp. No.	swelling/ compatibilizing cation	decomposition onset temperature (C)	weight loss between 100 and 300°C (% of total onium ion content)
1	dipentyl ammonium (secondary)	275	5.6
2	dimethyldodecyl ammonium (tertiary)	190	27.8
3	quaternary alkylammonium ^a	220	38.5

a. Claytone APA (montmorillonite complex) obtained from Souther Clay Products.

COMPARATIVE EXAMPLE 2

A nylon 6 nanocomposite of a layered material derivatized with an acidic omega-aminoacid cation was prepared by compounding, in a melt extrusion process, nylon 6 with about 3% (w/w) of montmorillite derivatized with protonated 11-aminoundecanoic acid cation. The montmorillonite complex was prepared, compounded, molded and tested according to the procedure of Example 1 except that an aqueous solution of 11-aminoundecanoic acid hydrochloride was used. The results of the tests are set forth in Table 4. For comparison purposes, nylon 6 was subjected to analysis of ultimate elongation, tensile modulus, tensile strength, and heat deflection under load. These results, together with comparable data for nylon 6 having montmorillnite dipentyl ammonium cation complex are set forth in the following Table 4.

WHAT IS CLAIMED IS:

1. Composite material comprising a polymer matrix which comprises a polymer matrix and dispersed platelet particles having an average thickness of less than 50 Å and a maximum thickness of about 100 Å, and having an onium chemical species bonded to them, said chemical species selected from the group consisting of onium compounds of the formula:



10 wherein:

R_1 is an organic radical having at least about 12 aliphatic carbon atoms and optionally including one or more heteroatoms, carbonyl functions or a combination thereof;

15 R_2 and R_3 are the same or different at each occurrence and are organic radicals at least one of which having at least about 5 carbon atoms and optionally including one or more heteroatoms, carbonyl functions or a combination thereof; and

20 R_4 , R_5 , R_6 and R_7 are the same or different and are organic radicals at least one of which has eight or more aliphatic carbon atoms and optionally including one or more heteroatoms, carbonyl functions or a combination thereof, said platelet particles being present in an amount less than about 60% by weight of the composite material.

2. Composite material of claim 1, wherein said platelet particles are derived from phyllosilicates.

3. Composite material of claim 2, wherein said phyllosilicates are smectites clay minerals.

4. Composite material of claim 3, wherein said swelling/compatibilizing agent is selected from the group consisting of primary and secondary ammonium cationic complexes of the formula:



wherein:

7. Composite material of claim 6, wherein said polymeric matrix comprises a polyamide, a polyester, a polyolefin, or a combination thereof.

8. Composite material of claim 7, wherein said
5 polymeric matrix comprises poly(ethylene terephthalate), poly(ethylene naphthalate), polyethylene, polypropylene, nylon 6, nylon 6,6, nylon 12 or a combination thereof.

9. An article of manufacture comprising a body,
10 said body fabricated, totally or in part, from a composite material comprising a polymer matrix which comprises a heat processible polymer and dispersed platelet particles having an average thickness of less than 50 Å and a maximum thickness of about 100 Å, and
15 having an onium chemical species bonded to them, said chemical species selected from the group consisting of onium compounds of the formula:



wherein:

20 R_1 is an organic radical having at least about more 12 aliphatic carbon atoms and optionally including one or more heteroatoms, carbonyl functions or a combination thereof;

R_2 and R_3 are the same or different at each
25 occurrence and are organic radicals having at least about 5 carbon atoms and optionally including one or more heteroatoms, carbonyl functions or a combination thereof; and

R_4 , R_5 , R_6 and R_7 are the same or different and are
30 organic radicals at least one of which has 8 or more aliphatic carbon atoms and optionally including one or more heteroatoms, carbonyl functions or a combination thereof, said platelet particles being present in an amount less than about 60% by weight of the composite
35 material.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 92/06732

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) * According to International Patent Classification (IPC) or to both National Classification and IPC IPC ⁵ : C 08 K 3/34, C 08 L 77/00, C 08 L 23/02						
II. FIELDS SEARCHED <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black; margin: 5px 0;">Minimum Documentation Searched †</div> <table style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 20%; border-bottom: 1px solid black;">Classification System</th> <th style="border-bottom: 1px solid black;">Classification Symbols</th> </tr> <tr> <td style="border-right: 1px solid black; padding: 5px;">IPC⁵</td> <td style="padding: 5px;">C 08 K, C 08 L 23/00, C 08 L 77/00</td> </tr> </table> <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black; margin: 5px 0;">Documentation Searched other than Minimum Documentation to the extent that such documents are included in the fields searched *</div>			Classification System	Classification Symbols	IPC ⁵	C 08 K, C 08 L 23/00, C 08 L 77/00
Classification System	Classification Symbols					
IPC ⁵	C 08 K, C 08 L 23/00, C 08 L 77/00					
III. DOCUMENTS CONSIDERED TO BE RELEVANT *						
Category *	Citation of Document, † with indication, where appropriate, of the relevant passages ‡	Relevant to Claim No. ‡				
P, X	EP, A1, 0 459 472 (KABUSHIKI KAISHA TOYOTA CHUO KENKYUSHO) 04 December 1991 (04.12.91), see page 3, line 3 - page 4, line 38; examples; claims.	1-10				
X	US, A, 4 889 885 (USUKI et al.) 26 December 1989 (26.12.89), see column 3, line 11 - column 9, line 41; examples; claims.	1-10				
A	Polymer Preprints, vol. 32, April 1991, American Chem. Soc. KAZUHISA YANO et al. "Synthe- sis and properties of poly- mide-clay hybrid", pages 65, 66 see Totality.	1-10				
<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>* Special categories of cited documents: †</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubt on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>† later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"Z" document member of the same patent family</p> </div> </div>						
IV. CERTIFICATION						
Date of the Actual Completion of the International Search <div style="text-align: center; font-size: 1.2em;">03 November 1992</div>		Date of Mailing of this International Search Report <div style="text-align: center; font-size: 1.2em;">25 NOV 1992</div>				
International Searching Authority <div style="text-align: center; font-weight: bold;">EUROPEAN PATENT OFFICE</div>		Signature of Authorized Officer <div style="text-align: center; font-weight: bold;">TENGLER e.h.</div>				

ANHANG

ANNEX

ANNEXE

zum internationalen Recherchen-
bericht über die internationale
Patentanmeldung Nr.

to the International Search
Report to the International Patent
Application No.

au rapport de recherche inter-
national relatif à la demande de brevet
international n°

PCT/US 92/06732 SAE 63495

In diesem Anhang sind die Mitglieder
der Patentfamilien der im obenge-
nannten internationalen Recherchenbericht
angeführten Patentdokumente angegeben.
Diese Angaben dienen nur zur Unter-
richtung und erfolgen ohne Gewähr.

This Annex lists the patent family
members relating to the patent documents
cited in the above-mentioned inter-
national search report. The Office is
in no way liable for these particulars
which are given merely for the purpose
of information.

La présente annexe indique les
membres de la famille de brevets
relatifs aux documents de brevets cités
dans le rapport de recherche inter-
national visée ci-dessus. Les renseigne-
ments fournis sont donnés à titre indica-
tif et n'engagent pas la responsabilité
de l'Office.

Im Recherchenbericht angeführtes Patentdokument Patent document cited in search report Document de brevet cité dans le rapport de recherche		Datum der Veröffentlichung Publication date Date de publication	Mitglied(er) der Patentfamilie Patent family member(s) Membre(s) de la famille de brevets	Datum der Veröffentlichung Publication date Date de publication
EP A1	459472	04-12-91	JP A2 4033955	05-02-92
US A	4889885	26-12-89	JP A2 1198645	10-08-89
			DE A1 3806548	15-09-88
			JP A2 63221168	14-09-88
			JP A2 63215775	08-09-88
EP A1	351337	17-01-90	BR A 8903428	13-02-90
			CN A 1039251	31-01-90
			DK A0 3446/89	12-07-89
			DK A 3446/89	13-01-90
			FR A1 2634215	19-01-90
			JP A2 2055745	26-02-90
			US A 4994518	19-02-91